



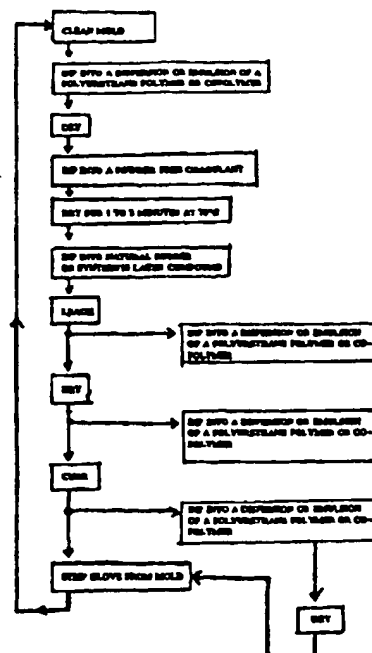
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

|   |           |   |
|---|-----------|---|
| <b>(51) International Patent Classification 6 :</b><br><b>B29C 41/14, 41/22, B32B 25/08, A61B 19/04</b>   | <b>A1</b> | <b>(11) International Publication Number:</b> <b>WO 96/23643</b><br><b>(43) International Publication Date:</b> 8 August 1996 (08.08.96)  |
| <b>(21) International Application Number:</b> PCT/US96/01388<br><b>(22) International Filing Date:</b> 26 January 1996 (26.01.96)<br><b>(30) Priority Data:</b><br>08/382,614      2 February 1995 (02.02.95)      US<br><b>(71) Applicant:</b> BAXTER INTERNATIONAL INC. [US/US]; One Baxter Parkway, Deerfield, IL 60015 (US).<br><b>(72) Inventor:</b> PLAMTHOTTAM, Sebastian, S.; 1496 Moonridge Court, Upland, CA 91784 (US).<br><b>(74) Agents:</b> STENZEL, Robert, A. et al.; One Baxter Parkway, Deerfield, IL 60015 (US). |           | <b>(81) Designated States:</b> JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).<br><br><b>Published</b><br><i>With international search report.</i><br><i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> |

**(54) Title:** A PROCESS FOR MAKING A GLOVE HAVING A POLYURETHANE COATING

**(57) Abstract**

The present invention relates to a multiple-dip process for producing a powder-free glove having a polyurethane coating. The method of this invention involves dipping a former into a powder-free aqueous dispersion or emulsion of a polyurethane polymer or copolymer to form a first layer; dipping the first layer while still on the former into a powder-free coagulant; dipping the first layer into a latex compound to produce a second layer; leaching the second layer in water; curing the first and second layers; and stripping the resulting glove from the former. Gloves produced according to this process can be made in a continuous fashion without interruption and are more economical than conventional processes used to make powder free gloves. The method of this invention does not include a halogenation step but rather employs environmentally friendly materials which do not pose toxicity of environmental issues.



**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

|    |                          |    |                                       |    |                          |
|----|--------------------------|----|---------------------------------------|----|--------------------------|
| AM | Armenia                  | GB | United Kingdom                        | MW | Malawi                   |
| AT | Austria                  | GE | Georgia                               | MX | Mexico                   |
| AU | Australia                | GN | Guinea                                | NE | Niger                    |
| BB | Barbados                 | GR | Greece                                | NL | Netherlands              |
| BE | Belgium                  | HU | Hungary                               | NO | Norway                   |
| BF | Burkina Faso             | IE | Ireland                               | NZ | New Zealand              |
| BG | Bulgaria                 | IT | Italy                                 | PL | Poland                   |
| BJ | Benin                    | JP | Japan                                 | PT | Portugal                 |
| BR | Brazil                   | KE | Kenya                                 | RO | Romania                  |
| BY | Belarus                  | KG | Kyrgyzstan                            | RU | Russian Federation       |
| CA | Canada                   | KP | Democratic People's Republic of Korea | SD | Sudan                    |
| CF | Central African Republic | KR | Republic of Korea                     | SE | Sweden                   |
| CG | Congo                    | KZ | Kazakhstan                            | SG | Singapore                |
| CH | Switzerland              | LI | Liechtenstein                         | SI | Slovenia                 |
| CI | Côte d'Ivoire            | LK | Sri Lanka                             | SK | Slovakia                 |
| CM | Cameroon                 | LR | Liberia                               | SN | Senegal                  |
| CN | China                    | LT | Lithuania                             | SZ | Swaziland                |
| CS | Czechoslovakia           | LU | Luxembourg                            | TD | Chad                     |
| CZ | Czech Republic           | LV | Latvia                                | TG | Togo                     |
| DE | Germany                  | MC | Monaco                                | TJ | Tajikistan               |
| DK | Denmark                  | MD | Republic of Moldova                   | TT | Trinidad and Tobago      |
| EE | Estonia                  | MG | Madagascar                            | UA | Ukraine                  |
| ES | Spain                    | ML | Mali                                  | UG | Uganda                   |
| FI | Finland                  | MN | Mongolia                              | US | United States of America |
| FR | France                   | MR | Mauritania                            | UZ | Uzbekistan               |
| GA | Gabon                    |    |                                       | VN | Viet Nam                 |

## A PROCESS FOR MAKING A GLOVE HAVING A POLYURETHANE COATING

### FIELD OF THE INVENTION

The present invention relates to a process of making a glove. More specifically, the present invention relates to a process of making powder-free gloves in a multiple dip process having a polyurethane coating.

### BACKGROUND OF THE INVENTION

Normally, natural rubber articles such as medical gloves, industrial gloves, condoms, etc. are made from latex by a dipping process. Traditionally, three dipping technologies have been used. The first type of dipping is straight dipping. Straight dipping can be used to make articles such as condoms, examination gloves, finger cots, etc. The process of straight dipping involves dipping a clean former into latex, drying the deposited film, and then dipping the former into latex again. The dipping and drying continues until the requisite number of layers is achieved. After the last dip, the latex is only partially dried and a bead rolled at the cuff edge or open edge of the article. Once the bead is made, the article is cured, leached and wet stripped from the former. In a dry stripping process, the article is dried after leaching/soaking, soaked with a release agent such as cornstarch, and removed from the former.

The second type of dipping is coagulant dipping. Coagulant dipping is more frequently used to produce surgical, examination and industrial gloves. As its name suggests, coagulant dipping employs the use of a coagulating agent, which can be a mono or bivalent metal salt such as calcium nitrate, calcium chloride, zinc nitrate, etc. The coagulant is usually deposited on the former before or after the dip in the latex.

Two types of coagulant dipping processes are used.

See R. Waterman, R. Mausser, E. Miller, Materials and Processes for Latex Compounding (R.T. Vanderbilt Company, Inc., New York, 1972), p. 106. The first coagulant dipping process is the Anode process. In the  
5 Anode process, a cleaned former is dipped into a coagulant solution or slurry, dried, and then dipped into latex. The dried coagulant breaks the latex emulsion and causes the rubber articles to coalesce and form a film on the former. The film is then leached in  
10 water to remove the water soluble components, such as excess coagulant. After leaching, the film is dried, then cured, and the article stripped from the former.

The second type of coagulant dipping process is the Teague process. In the Teague process, a cleaned  
15 former is first dipped to latex, then into a coagulant solution and then into latex. The remaining steps are similar to the Anode Process.

The third type of dipping is heat sensitive dipping. Heat sensitive dipping involves the use of a  
20 heated former. The latex is compounded to make it heat sensitive when contacted with the heated former. See Blackley, High Polymer Latices, Vol. 1 and 2, McClaren & Son, Ltd. (1966) pg. 532. The deposit builds up around the former as heat is conducted away into the  
25 surrounding latex. Id. The thickness of the deposit obtained depends upon several factors, notably the degree of heat sensitivity of the latex, the temperature of the former and the heat capacity of the former. Id.

30 The above processes typically incorporate the use of powder, such as talc, cornstarch, etc. Powder is either included in the coagulant, or applied to the cured article prior to stripping. The addition of the powder serves two important  
35 purposes. First, powder reduces the tackiness or stickiness of the glove and facilitates the removal of

the glove from the former. With gloves, removal of the  
from the former is often difficult because cured latex  
gloves tend to be tacky and adhere to the former.  
However, powder reduces the tackiness or stickiness of  
5 the gloves and improves stripping. Second, powder  
facilitates donning.

While the use of powder reduces tackiness and  
facilitates donning, it causes many problems. The main  
problem is that the completed glove contains a great  
10 deal of residual powder. With surgical gloves, there  
is a risk that this powder could escape from gloves and  
contaminate the surgical field if the gloves were to  
rip or puncture. Another problem associated with the  
use of powder is that the powder remains on the former  
15 after the formation of an glove. Because the powder  
remains on the former, the former must be cleaned after  
each and every glove. Because of all of these  
problems, several attempts have been made to eliminate  
the use of powder in the construction of rubber gloves.

20 Several processes are known in the art for making  
powder free gloves. One way to make a natural rubber  
latex article powder free is via halogenation, normally  
with chlorine, in a batch process. The chlorination  
process has been used frequently in the art to remove  
25 powder from the surface of gloves and to facilitate  
donning. For example, U.S. Patents 3,411,982 and  
3,740,262 disclose using halogenation to make the  
surface of a rubber glove slippery. U.S. Patent  
4,304,008 uses halogenation to facilitate donning in  
30 lieu of powder lubricants in rubber articles. For  
instance, U.S. Patent 3,740,262 discloses a glove that  
has been halogenated to provide a powder-free rejecting  
outer surface and powder-free accepting inner surface.

While the halogenation process removes powder and  
35 facilitates donning, halogenated products have several  
drawbacks. First, gloves produced using halogenation

are more expensive to produce due to the number of halogenation steps, turning steps, and drying process involved in the manufacture. Also, halogenated products tend to discolor and age poorly, both in storage and in use. Furthermore, halogenated products may become hard, brittle, and brown in color when exposed to air. Additionally, chemicals used for halogenation such as chlorine are considered to be toxic chemicals thereby presenting disposal and environmental issues.

Several methods for making powder-free gloves is known in the art. For example, U.S. Patent 4,310,928 discloses a talc free surgeon's glove that is made by first dipping a former into a coagulant solution containing a lipo compound and a surfactant. The former is then dipped into latex to form the glove. U.S. Patent 4,499,154 discloses a powder free rubber article made from rubber which has a hydrophilic inner coating which is coated with surfactants and silicone. The patent also discloses a method for making such a powder free rubber article, however, the number of steps involved in this process makes it unduly expensive and the lower molecular weight component (surfactants and silicone) could cause contamination.

Other examples include U.S. Patent 5,138,718 which discloses a method of making powder free gloves, finger stalls, and other protective articles using latex and microcapsules. The microcapsules are dispersed and arranged in the latex to form a concentration gradient, with the concentration of the microcapsules increasing progressively from the outer surface to the inner surface of the article. The microcapsules can contain a pharmaceutically active substance such as nonoxynol, moroxydine hydrochloride, or vidarabine to provide viricidal activity against diseases such as AIDS or

herpes. See U.S. Patent 5,024,852.

For several decades now, the growth of the polyurethane art has been tremendous. Due to growth, numerous kinds of polyurethane polymers are known.

5 Polyurethanes include those polymers containing primarily urethane groups, regardless of what the rest of the molecule may be. J.H. Saunders and K.C. Firsch, Polyurethanes, Chemistry and Technology, Part I, Interscience Publishers (1965). Usually these polymers  
10 are obtained by the combination of a polyisocyanate with reactants which have at least some hydroxyl groups, eg., polyethers, castor oil, and simple glycols. Other reactive groups may also be present, such as amino and carboxy. Thus a typical  
15 "polyurethane" may contain, in addition to urethane groups, aliphatic and aromatic hydrocarbon, ester, ether, amide and urea groups. These polymers are also sometimes called simply "urethanes," and sometimes "isocyanate polymers."

20 Often, urethanes are considered esters of the unstable carbamic acid, or amide esters of carbonic acid:

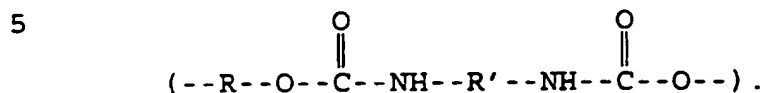


and the urethane group has the characteristic configuration:



Polyurethanes can be formed by a variety of methods, although the most widely used production method is the reaction of di- or polyfunctional hydroxyl compounds such as hydroxyl-terminated  
35 polyesters or polyethers, with di- or polyfunctional

isocyanates. The general structure of a linear polyurethane derived from a dihydroxy compound, HOROH, and a diisocyanate, OCNR'NCO, can be represented by the following general formula:



The functionality of the hydroxyl-containing component as well as of the isocyanate can be increased to three or more to form branched or cross-linked polymers. Other structural changes can be made at will, also. For example the nature of R may be changed, such as in molecular weight and type (polyether, polyester, simple glycol), and mixtures of these polyhydroxy compounds can be used. Similarly, the nature of the R' may be altered, as in the change from naphthalene diisocyanate to hexamethylene diisocyanate. For these reasons the polyurethanes are almost unique in that cross linking, chain flexibility, and intermolecular forces can be varied widely and almost independently. It is to be expected, then, that the polyurethanes include fibers, soft and hard elastomers, flexible and rigid foams, coatings for many purposes, and highly cross linked plastics. Id.

25 As stated above, many polyurethane resin systems are known and new resins are continuously being formulated. There is a great deal of prior art describing the polyurethane polymer art and no attempt



will be made here to even summarize this art. However, a brief listing of some polyurethane patents is listed below:

U.S. Patent 3,828,238 discloses hydrophilic  
5 polyurethane polymers prepared from resins having low ratio of carbon to oxygen to nitrogen or having ionic, quaternary ammonium or salt groups in the resin backbone and a low amount of isocyanate.

U.S. Patent No. 3,975,350 discloses a hydrophilic  
10 carrier system comprising a polyurethane combined with an active agent.

U.S. Patent No. 4,156,066 and 4,156,067 disclose polyurethane polymers having a molecular weight of about 6,000 and having lactone and hydroxyl groups in  
15 the polymer backbone.

U.S. Patent No. 4,255,550 discloses water insoluble polyurethane polyether polymers that are soluble in ethanol at a pH of 11, have a molecular weight above 6,000 and have carboxylate groups and  
20 hydroxyl groups in the polymer backbone.

U.S. Patent No. 4,408,023 discloses hydrophilic polyurethane dicacrylate compositions. U.S. Patent No. 4,424,305 discloses surgical implants formed from polyurethane diacrylate compositions and U.S. Patent  
25 No. 4,439,583 discloses canulae formed from polyurethane diacrylate compositions.

U.S. Patent No. 4,439,584 discloses hydrophilic

polyurethane diacrylate compositions useful for forming gas and permeable membranes. U.S. Patent 4,439,585 discloses polyurethane diacrylate compositions useful as carriers for pharmacologically active agents.

5 U.S. Patent No. 4,451,635 discloses polyurethane quaternary ammonium salt compositions obtained by reacting a solution of one or more organic chlorides and one or more hydrophilic polyurethane resins dissolved in a water-miscible organic solvent in the  
10 presence of a strong base.

U.S. Patents Nos. 4,454,309 and 4,490,423 and 4,496,535 disclose hydrophilic polyurethane polyene compositions. The compositions are obtained by the reaction of one or more polyenes in the presence of one  
15 or more hydrophilic polyurethanes.

U.S. Patent No. 4,780,512 discloses hydrophilic polyurethane acrylate compositions.

U.S. Patent No. 4,743,673 discloses hydrophilic carboxyl polyurethanes. Traditionally, carboxyl  
20 polyurethanes have been difficult to prepare.

U.S. Patent No. 4,789,720 discloses hydrophilic polyurethane polymers prepared from a combination of certain alkylene glycols. The polyurethane have improved dimensional stability, mechanical strength,  
25 and have an average molecular weight of from about 10,000 to about 200,000.

U.S. Patent Nos. 4,810,582 and 4,798,876 disclose

a water absorptive polyurethane polyene composition.

U.S. Patent No. 4,945,149 discloses a coating composition for forming a substantially non-porous moisture-permeable coating layer or film of a  
5 hydrophilic polyurethane resin. The hydrophilic polyurethane resin comprises a polyol combination and a polyisocyanate compound or prepolymer of a polyurethane resin.

U.S. Patent No. 4,119,094 discloses a substrate  
10 coated with a polyvinyl pyrrolidone-polyurethane interpolymer. The coating has a very low coefficient of friction.

U.S. Patent No. 4,990,357 discloses a coating composition for an article comprising a uniform blend  
15 of an elastomeric segmented hydrophilic polyetherurethane and a hydrophilic polymer, such as polyvinylpyrrolidone.

U.S. Patent No. 4,100,309 discloses a substrate coated with a polyvinylpyrrolidone-polyurethane  
20 interpolymer.

U.S. Patent No. 4,670,330 discloses a water-insoluble, hydrophilic polyurethane resin having hydrophilic groups and/or hydrophilic segments in the main chains and/or side chains.

25 U.S. Patent No. 4,783,857 discloses a moisture permeable glove utilizing a polyurethane film.

The object of the present invention is to provide

a process  
for making a powder-free glove having a polyurethane  
coating using multiple-dip coating technologies with  
carefully engineered functional inner and outer layers.  
5 Gloves made in this manner can be produced in a  
continuous fashion, with substantial economic savings,  
and added features and benefits. In addition,  
environmentally friendly materials and processes can be  
used if water borne systems are selected for use in  
10 conjunction with this process.

#### SUMMARY OF THE INVENTION

The present invention provides a process of making  
a powder-free glove having a polyurethane coating using  
a multiple dip process. In addition, this process can  
15 be used to make powder-free articles such as surgical  
and examination gloves, catheters and condoms. The  
method disclosed in this application can also be used  
to construct other medical articles such as finger  
stall, surgical operative fields, aprons, bibs, and  
20 caps.

A process of making a powder-free glove using a  
multiple-dip process comprises the following steps:

dipping a former of the desired shape of the glove  
into a powder-free dispersion or emulsion of a  
25 polyurethane polymer or copolymer to form a first  
layer; dipping the first layer while still on the

former into a powder-free coagulant; dipping the first layer into a latex compound to produce a second layer; leaching the second layer in water; curing the first and second layers; and stripping the resulting glove  
5 from the former.

The above process of this invention can further comprise the step of coating the glove with a lubricating, powder-free polymer either before or after curing. The lubricating powder-free polymer is added  
10 to facilitate donning as well as to reduce the tackiness of the article to facilitate its removal from the former.

The process of this invention can be used to make a powder-free, multi-layered glove. The multiple-dip  
15 process of this invention can be carried out in a continuous fashion without interruption thereby making this process more economical than the traditional processes used to make powder-free gloves. Also, the process of this invention uses environmentally friendly  
20 materials and does not employ the use of halogens such as chlorine.

#### DESCRIPTION OF THE DRAWINGS

Figure 1 shows in flow-chart fashion, the process of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a multiple dip process for producing a powder-free polyurethane coated glove. As used in the specification and appended  
5 claims, "powder-free" means that the glove has been manufactured to eliminate most, if not all, of the powder on the surface of the glove.

To produce a powder-free glove, a former in the desired shape is first dipped into a powder-free  
10 polymer composition to form a film or first layer. The former (or mold) used is in a variety of sizes and shapes corresponding to the various hand sizes for which the gloves are intended. To facilitate the removal of the glove from the former, Halar®, Kynar®,  
15 and Teflon® coated molds can be used. Formers that are contoured and have textured to highly polished ceramic or porcelain surfaces or fluorocarbon coatings can be used. In addition, glass, hard woods, and plastic formers can also be used.

20 The polymer composition comprises a polymer suspension. The polymer suspension used in the composition is in the form of a aqueous dispersion or emulsion. Methods for making polymer aqueous dispersions and emulsions are well known in the art.

25

Additives can be added to the dispersion or emulsion. For example, defoamers, which are used to

eliminate bubbles can be used. Also, surfactants can be added to improve the wetting characteristics or stability of the dispersion or emulsion. A surfactant is defined as a compound that reduces surface tension  
5 when dissolved in water or water solutions. Non-ionic, cationic, or anionic surfactants well known in the art can be used as long as the surfactant does not destabilize the polymer.

The polymers contemplated for use in the polymer  
10 composition are polyurethanes. As discussed in the "Background of the Invention," polyurethanes comprise of urethane groups, regardless of what the rest of the molecule may be. Many types of polyurethane polymers and copolymers are known in the art and can be used in  
15 this invention. For examples, a polyurethane known as U50, available from B.F. Goodrich Company, Cleveland, Ohio can be used. U50 is a medium-soft, light fast, aqueous aliphatic urethane dispersion. Another polyurethane that can be used is Witcobond® W-404,  
20 available from the Witco Corporation, Houston, Texas. Witcobond® W-404 is a high-solid, semi-colloidal aliphatic polyurethane dispersion. However, the preferred polyurethanes are those that have surface modified end groups which facilitate easy removal of  
25 the resultant glove from the former.

Polyurethanes that have been modified with surface-modified end groups are available from The

Polymer Technology Group Incorporated, Emeryville, California, USA. The surface modified end groups are oligomeric. Surface modification via these oligomeric end-groups is easily adapted to the synthesis of

5 polymers which normally incorporate a low molecular weight control. By restricting the surface-modifying moieties to the termini of linear based polymers such as polyurethanes, changes to the base polymer's bulk properties are minimized. Robert S. Ward and Kathleen

10 A. White, "Development of A New Family of Polyurethanesurea Biomaterial," Topical Symposium VIII, Materials in Clinical Applications, Florence, Italy, July 1994. Examples of oligomeric end groups that can be used are dodecyl amine, polydimethylsiloxane amine,

15 polyethyleneoxide-amines or alcohols, just to name a few. The method for making such polyurethanes is described in "Development of A New Family of Polyurethanesurea Biomaterial," by Robert S. Ward and Kathleen A. White, Topical Symposium VIII, Materials in

20 Clinical Applications, Florence, Italy, July 1994, hereby incorporated by reference.

Additionally, the polymer dispersion or emulsion used in this invention is substantially free of solvent. As used in this specification, "substantially

25 free of solvent" means that low levels of solvent can be added to the dispersion or emulsion without causing destabilization. A solvent is a substance capable of



dissolving another substance (a solute) to form a uniformly dispersed mixture (a solution) at the molecular or ionic size level. Solvents may be polar or nonpolar. One skilled in the art would recognize  
5 that high levels of solvent cause water-borne systems such as dispersions and emulsions to destabilize.

Once the polyurethane composition is prepared, the former is immersed or dipped in the composition to form a film or first layer. After several seconds, the  
10 former is withdrawn from the polyurethane dispersion or emulsion, subjected to a wavy motion to distribute the coating uniformly around the former and dried. After drying, the first layer is dipped into a powder-free coagulant.

15 The powder-free coagulant can be water or alcohol based. While water or alcohol based coagulants are most commonly used, heat-sensitive coagulation systems can also be used. In a heat sensitive system, a heated former is employed. The latex is compounded in order  
20 to make it heat sensitive when contacted with the heated former. The deposit builds up around the former as heat is conducted away into the surrounding latex. Blackley, High Polymer Latices, Vol. 1 and 2, McClaren & Son, Ltd. (1966) pg. 532. The thickness of the  
25 deposit obtained depends upon several factors, notably the degree of heat sensitivity of the latex, the temperature of the former and the heat capacity of the

former. Id. Heat sensitivity can be induced by any standard methods, however, compounding with polyvinyl methyl ether is the most useful method, because this substance is very effective and yet tends to enhance  
5 the room temperature stability of latex compounds. Id.

After withdrawal of the former from the coagulant solution, the first layer is dried for 1 to 2 minutes at 70°C. Once dried, the first layer is capable of inducing coagulation when the former is dipped into a  
10 latex compound.

After the formation of the first layer, the former is then dipped into a latex compound to form a second layer. The latex can be any coagulatable natural or synthetic latex compound, coagulatable natural or  
15 synthetic rubber latices or styrenic block copolymer dispersions known in the art. Conventional formulations for the preparation of latex are well known in the art and one skilled in the art would be readily able to vary the formulations and conditions of  
20 curing and the like to suit the particular latex being used as well as the final article desired. Precured, partially cured, or non-cured latex can be used. Additionally, the latex may contain conventional compounding ingredients commonly utilized. Specific  
25 examples are given in U.S. Patent 3,411,982, hereby incorporated by reference.

When the former is dipped into the latex compound, the dried first layer induces coagulation of the latex to produce a uniform coagulated deposit of the latex on the former. The length of time the former is immersed  
5 in the latex and the concentration of the coagulant determines the thickness of the article. The longer the dwell time period, the greater the wall thickness of the article, and vice versa. Articles produced according to the method of this invention typically  
10 have a thickness of between 4 to 15 mils.

The former is removed from the latex with a coating of gelled latex adhering to it. The former is placed in a water bath to leach out water soluble components such as proteins, electrolytes, etc. The  
15 temperature of the water bath is between 40-60°C.

After leaching, the second layer is either dried or coated with a lubricating polymer. If dried, then the first and second layers are cured. As used in this invention, the term "curing" also includes "fusing" or  
20 "fusion" as some types of polymers require fusing instead of curing. For example, thermoplastic elastomers such as the copolymers poly(styrene-b-isoprene-b-styrene) (SIS), poly(styrene-b-butadiene-b-styrene) (SBS), and poly(styrene-b-ethylene propylene-  
25 b-styrene) (SEPS) require fusing. Typically, however, curing is employed. The length of time required for curing depends upon the polymers selected, however,

most polymers can be cured in about 5 to 10 minutes at 138°C. After curing, the resulting article is allowed to cool and is removed from the former.

A lubricating polymer can be coated on the article  
5 to facilitate donning and the removal of the glove from the former. The lubricating polymer used in this invention can be in the form of a dispersion or emulsion and is applied by either dipping or spraying. Lubricating polymers that can be used in this invention  
10 include those polymers which will provide a coating that will anchor well to the article, will facilitate donning and will assist in the removal of the glove from the former. The polyurethane polymer used to form the first layer can be used as the lubricating polymer.  
15 However, one is not limited to using the same polymer as was used to form the polymer composition. Different polymers can be used. For example, the lubricating polymers that can be used can be homopolymers, copolymers (by which is meant a polymer of two or more  
20 monomers), mixtures of homopolymers and copolymers. Examples of suitable polymers that can be used include vinyl polymers and copolymers, acrylic acid and methacrylic acid polymers and copolymers, styrenic block copolymers, polyurethanes and the like. Examples  
25 of vinyl polymers that can be used include: vinyl chloride, vinyl acetate, vinyl propionate and the like. Example of acrylic acid polymers that can be used

include alkyl acrylate polymers and copolymers such as ethyl acrylate, methyl acrylate, propyl acrylate, methylethacrylate and the like. Examples of styrenic block copolymers include: styrene-butadiene, styrene-  
5 ethylene-butylene, styrene-ethylene-propylene, styrene-isoprene, and the like. One skilled in the art would recognize that various polymers could be used to facilitate the donning and the removal of the article from the former.

10 The lubricating polymer can be applied either before the drying of the second layer, after the drying of the second layer but before curing, or after curing. When the lubricating polymer is applied, it will add additional layers to the already multi-layered article.  
15 After the lubricating polymer is added, it is allowed to stand and dry or is dried in an oven. One skilled in the art would recognize that the conditions required for drying the lubricating polymer in an oven vary based on the type of lubricating polymer employed. If  
20 the lubricating polymer is added to the glove prior to curing, the lubricating polymer may be dried and the glove cured in one step. If the lubricating polymer is applied after the article is cured, then the lubricating polymer must be dried. Once dried, the  
25 glove can be stripped from the former.

In addition to the lubricating polymer, certain additives such as emulsion silicones can also be used

to further enhance the donning and the release of the article from the former. A silicone is generally defined as a compound that includes siloxane polymers which are based on a structure including alternate  
5 silicon and oxygen atoms, with organic groups attached to the silicon. The emulsion silicones used in this invention can be included in the polyurethane composition applied as the first layer, the latex used to form the second layer or in the lubricating polymer.  
10 Examples of suitable silicones that can be used include polydimethylsiloxane (PDMS), Dow Corning Silicone Emulsion 365, and the like. Generally, adding less than 2% of these silicones to the respective polymer formulation will be sufficient to improve the donning  
15 and release of the article.

Stripping of the glove from the former turns the glove inside out so that the first layer is on the outside and the latex or lubricating layer is on the inside. The stripping process does not require any  
20 powder to release the glove from the former. Additionally, the resultant glove does not exhibit any tackiness.

The process of this invention results in multi-layered, powder-free gloves. Gloves produced according  
25 to this method can be easily removed from a former, are not tacky and exhibit good dry donning characteristics. Articles that can be made according to the method of

this invention in addition to gloves includes:  
catheters and condoms.

Gloves produced according to this invention have many features and benefits. Articles made according to the method of this invention have numerous advantages because they can be made in a continuous fashion with significant economic savings when compared to the conventional processes. The conventional processes used to make powder-free gloves are more expensive due to the number of halogenation, turning and drying steps involved in the manufacture. Gloves produced according to this method are easily removed from the former, not tacky, exhibit good donning characteristics, and are powder-free. The process of this invention eliminates a number of these steps.

A further advantage of this invention is that the process uses environmentally friendly materials. Unlike other processes used to make powder-free gloves, the process of this invention does not include a halogenation step. The halogenation process involves the use of toxic chemicals such as chlorine, which raises numerous disposal and environmental issues. In addition, halogenated products tend to discolor and age poorly both in storage and in use.

By way of example, and not limitation, examples of the present invention will now be given.

Example 1

A powder-free, Styrene-Isoprene-Styrene (SIS) glove was made by dipping a hand specific bisque form into a urethane dispersion having surface modified end groups such as WUWB 23115/S10 available from The Polymer Technology Group, (6.5% solids), and then into a methanol powder-free coagulant. The coating was dried and the former dipped into a styrene-isoprene block copolymer dispersion, such as DPX 546 available from Dexco Polymers. A thick deposit was formed on the coating which was next leached in warm water (50°C). A second coating of the urethane dispersion was applied by dip coating. The formed glove was fused at 71-93°C for about 20 minutes by slowly increasing the temperature of the oven from about 71 to 93°C. After cooling, the glove was stripped from the former. The glove showed good donning characteristics. The coating showed excellent anchorage to the SIS glove and was powder free. There was no sign of stickiness on either side. The user side of the glove looked glossy and smooth and the other surface replicated the surface features of the mold.

Example 2

An aqueous hydrophilic polyurethane dispersion, having surface modified end groups such as WUWB-23316/S5, available from The Polymer Technology Group,



containing 19.5% by weight of solids was diluted to 6.4% solids with DI water. Sufficient amount of Surfynol TG was added to this dispersion to sufficiently wet the ceramic forms used in making the gloves. About 18 g of Surfynol TG in about 7.46 Kg of dispersion seems to wet the mold in this case. A warm (40-50°C) textured ceramic ambi mold is dipped into this dispersion, and the coating is allowed to distribute evenly on the former using a wavy hand motion. The coating is dried in the oven at about 70°C for about five minutes. The coated former is then dipped into a methanol based powder free coagulant dispersions to slightly above the level of the coating. After drying the coagulant, the former is then dipped into natural rubber latex glove compound to the level of the first coating. The deposited film is then leached in warm water (37 to 54°C), and then a deposit of polyurethane is applied by dipping the level of the latex deposit. The formed glove is then cured at 138°C for about 10 minutes. The formed and cured glove is then stripped from the former in a conventional manner.

### Example 3

The polyurethane dispersion of Example 2 was diluted to 5.9% solids and the glove formed as detailed in example 4.

Example 4

To produce a beaded powder free urethane coated glove, the procedure of example 2 was followed except that the coatings were applied about 1/2 inch below the coagulant and latex deposit, and a bead was rolled in a conventional manner. Other aqueous polyurethanes such as Witcobond® W-404, a high solid, semi-colloidal aliphatic dispersion, available from Witco Corporation could also be used.

Although the invention has been described primarily in connection with the special and preferred embodiments, it will be understood that it is capable of modification without departing from the scope of the invention. The following claims are intended to cover all variations, uses, or adaptations of the invention, following, in general, the principles thereof and including such departures from the present disclosure as come within known or customary practice in the field to which the invention pertains, or as are obvious to persons skilled in the field.

## I CLAIM:

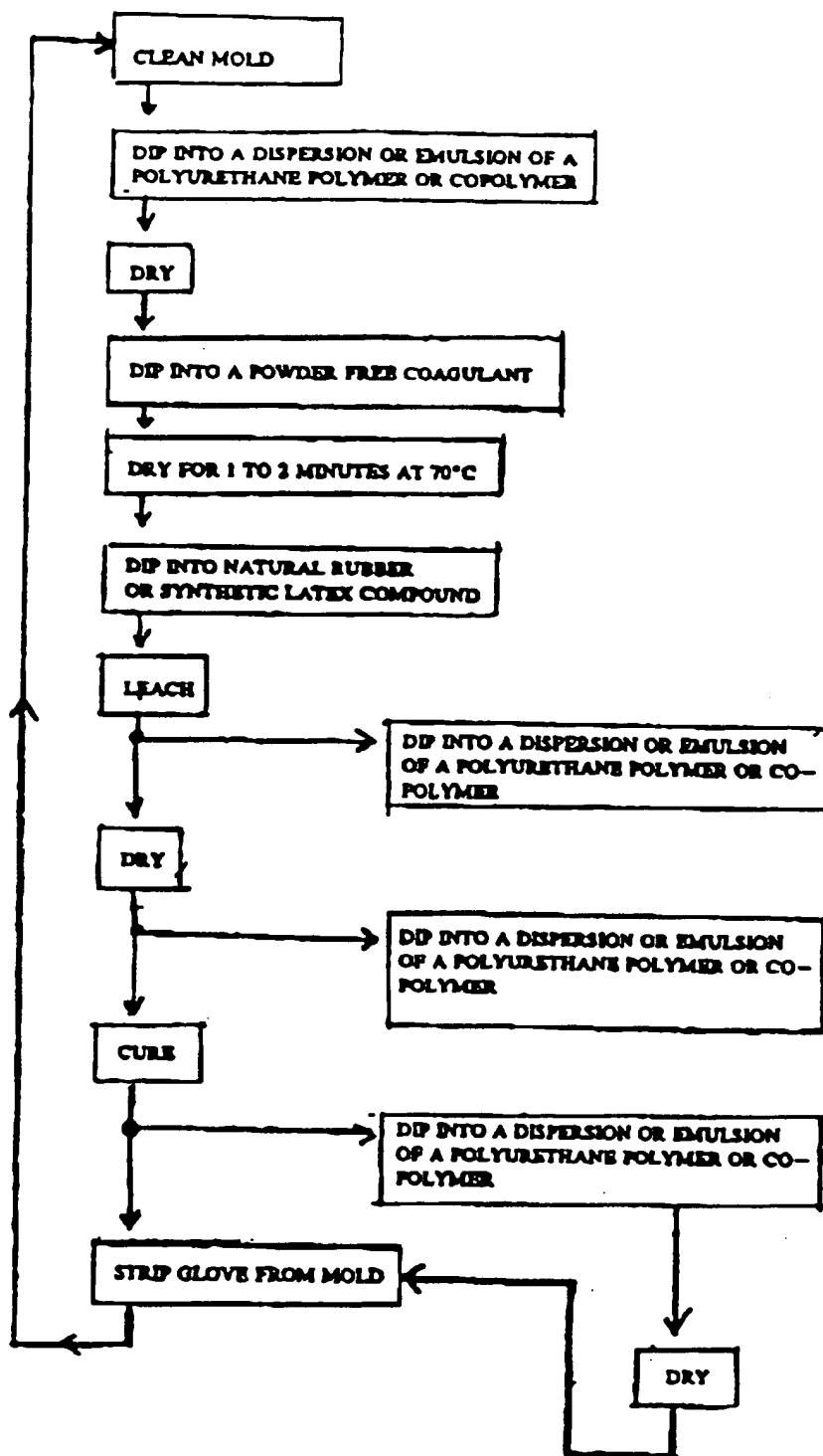
1. A multiple dip process for making a powder-free glove, the process comprising the steps of:

- 5 (a) dipping a former in the shape of a glove into an aqueous dispersion or emulsion of polyurethane polymer or copolymer to form a first layer;
- 10 (b) dipping the first layer while still on the former into a powder-free coagulant;
- (c) dipping the first layer while still on the former into a latex compound to produce a second layer;
- 15 (d) leaching the second layer in water;
- (e) curing the first and second layers; and
- (f) stripping the resulting glove from the former.
- 20 2. The process of claim 1 further comprising the step of applying a lubricating, powder-free polymer to the second layer before curing.
- 25 3. The process of claim 1 further comprising the step of applying a lubricating, powder-free polymer to the glove prior to stripping but after curing, and drying the lubricating polymer.
4. The process of claim 1 where the powder-free coagulant is water or alcohol based.
- 30 5. The process of claim 4 wherein the alcohol is methanol.
6. A multiple dip process for making a powder-free glove, the process comprising the steps of:
- (a) dipping a former of the desired shape of

- the glove                      into a powder-free aqueous  
dispersion or emulsion of  
polyurethane polymer or copolymer;
- 5                      (b) dipping the first layer while still on  
the former                      into a powder-free coagulant;
- (c) dipping the first layer while still on  
the former                      into a latex compound to produce a  
second layer;
- 10                      (d) leaching the second layer in water;
- (e) applying a lubricating, powder-free  
polyurethane                      polymer or copolymer;
- (f) curing the first and second layers; and
- (g) stripping the resulting article from the  
former.
- 15                      7. A multiple dip process for making a powder-  
free glove, the process comprising the steps of:
- (a) dipping a former of the desired shape of  
the glove                      into a aqueous dispersion or  
emulsion of polyurethane polymer or  
20                      copolymer;
- (b) dipping the first layer while still on  
the former                      into a powder-free coagulant;
- (c) dipping the first layer while still on  
the former                      into a latex compound to produce a  
25                      second layer;
- (d) leaching the second layer in water;
- (e) curing the first and second layers; and
- (f) applying a lubricating, powder-free  
polyurethane                      polymer or copolymer;
- 30                      (g) drying the lubricating polymer; and
- (h) stripping the resulting glove from the  
former.

1/1

FIGURE 1



# INTERNATIONAL SEARCH REPORT

Internat. Application No.  
PCT/US 96/01388

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 B29C41/14 B29C41/22 B32B25/08 A61B19/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 B29C B32B A61B A41D C08C C08J A61F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No. |
|------------|---|-----------------------|
| Y          | US,A,5 088 125 (CHRISTOPHER W. ANSELL ET AL) 18 February 1992<br>see column 5, line 21 - line 28; example 1<br>---                  | 1-7                   |
| P,Y        | EP,A,0 640 623 (SMITH & NEPHEW INC.) 1 March 1995<br>see column 3, line 7 - line 11; claims 1,2,9,10<br>---                         | 1-7                   |
| Y          | WO,A,94 20574 (BAXTER INTERNATIONAL INC.) 15 September 1994<br>see page 3, line 9 - line 29<br>see page 8, line 21 - line 33<br>--- | 1-7                   |
| Y          | WO,A,89 04647 (SUZANNE STILLMAN) 1 June 1989<br>see page 12, line 8 - line 21<br>---  | 1-7                   |
|            | -/--  |                       |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

24 June 1996

Date of mailing of the international search report

03.07.96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+ 31-70) 340-3016

Authorized officer

Van Nieuwenhuize, O

# INTERNATIONAL SEARCH REPORT

Internat. I Application No

PCT/US 96/01388

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No. |
|------------|--|-----------------------|
| A          | <p>EP,A,0 300 814 (SURGIKOS INC.) 25 January 1989<br/> see page 3, line 56 - page 4, line 2;<br/> claims 1,8; example 3<br/> -----</p> | 2,6                   |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Internal 1 Application No

PCT/US 96/01388

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
|---|---------------------|----------------------------|---------------------|
| US-A-5088125                              | 18-02-92            | AU-B- 605585               | 17-01-91            |
|   |                     | AU-B- 1623688              | 02-12-88            |
|   |                     | DE-A- 3880488              | 27-05-93            |
|   |                     | EP-A, B 0360805            | 04-04-90            |
|   |                     | WO-A- 8808311              | 03-11-88            |
|   |                     | JP-T- 3502529              | 13-06-91            |
|   |                     | US-A- 5272771              | 28-12-93            |
| -----                                     |                     |                            |                     |
| EP-A-640623                               | 01-03-95            | AU-B- 6871594              | 16-02-95            |
|   |                     | CA-A- 2128670              | 06-02-95            |
|   |                     | JP-A- 7062003              | 07-03-95            |
|   |                     | ZA-A- 9405853              | 05-04-95            |
| -----                                     |                     |                            |                     |
| WO-A-9420574                              | 15-09-94            | CA-A- 2134074              | 15-09-94            |
|   |                     | EP-A- 0643743              | 22-03-95            |
|   |                     | JP-T- 7506642              | 20-07-95            |
| -----                                     |                     |                            |                     |
| WO-A-8904647                              | 01-06-89            | AU-B- 2727588              | 14-06-89            |
| -----                                     |                     |                            |                     |
| EP-A-300814                               | 25-01-89            | US-A- 4853978              | 08-08-89            |
|   |                     | AT-T- 113813               | 15-11-94            |
|   |                     | AU-B- 604342               | 13-12-90            |
|   |                     | AU-B- 1925188              | 27-01-89            |
|   |                     | CA-A- 1302007              | 02-06-92            |
|   |                     | DE-D- 3852067              | 15-12-94            |
|   |                     | DE-T- 3852067              | 16-03-95            |
|   |                     | ES-T- 2063037              | 01-01-95            |
|   |                     | JP-A- 1043250              | 15-02-89            |
|   |                     | JP-B- 3044527              | 08-07-91            |
| -----                                     |                     |                            |                     |